



Dynamic Mechanical Analysis of E-Beam and Thermally Curable IPN Thermosets

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Steven H. McKnight

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Abstract

Interpenetrating polymer network (IPN) materials possess unique properties that can be exploited for multicomponent composite armor systems, including toughness and thermal stability. E-beam curing of composites and adhesives offers advantages, such as reduced cure shrinkages, over traditional autoclave processing by curing multiple resins through the thickness for thick-section composites in a single step. Because of the complexity and thickness of composite integral armor structures, e-beam curing is an attractive processing method for Future Combat System applications, and the development of these new resins permits this approach. This research seeks to discern the differences in viscoelastic behavior between traditional thermal and e-beam curing in IPN resins, as these viscoelastic characteristics may prove important for composite integral armor applications.

Acknowledgments

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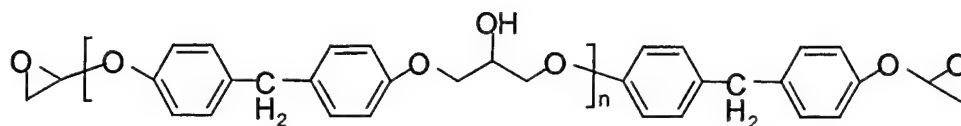
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1. Introduction

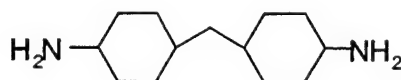
Polymer composites and adhesively bonded hybrid composite structures (e.g., composite-ceramic integral armor) are promising candidates for ultra-lightweight structural armor for Future Combat Systems (FCS). The development of composite resins for low-cost processing with improved properties will speed insertion of lightweight materials into FCS platforms. The processing and performance shortfalls in suitable resins may be addressed through exploitation of new electron beam (e-beam) curable systems including recently developed interpenetrating polymer network (IPN) materials. IPNs are polymers that are formed from the independent polymerization of two or more distinct networks, which results in unique molecular and physical microstructures offering improved properties [1]. The IPN materials are demonstrated to possess unique properties that can be exploited for multicomponent composite armor systems, including toughness and thermal stability. E-beam curing of composites and adhesives offers advantages, such as reduced cure shrinkages, over traditional autoclave processing by curing multiple resins through the thickness of thick-section composites in a single step. Because of the complexity and thickness of composite integral armor structures, e-beam curing is an attractive processing method for FCS applications and the development of these new resins permit this approach. This research seeks to discern the differences in viscoelastic behavior between traditional thermal and e-beam curing in IPN resins, as these viscoelastic characteristics may prove important for composite integral armor applications.

2. Materials

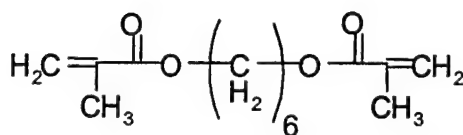
Dalal and Palmese previously developed the IPN formulation and cure routes [2]. The IPN formulation consisted of an epoxy network—diglycidyl ether of bisphenol F (DGEBF) (EEW = 170 g/mol) cured with bis(p-aminocyclohexyl) methane (EEW = 52.5 g/mol)—coupled to a free radical methacrylate network (1,6-hexanediol dimethacrylate [HDDMA]). The HDDMA free radical crosslinking reaction mechanism was initiated either via e-beam or thermal using the organic peroxide initiator 2,5-dimethyl-2,5-di-(t-butylperoxy) hexane. To couple the epoxy and methacryl networks together, a partial esterification reaction was used to convert an epoxy functionality of triphenylolmethane triglycidyl ether (TMTE) (EEW = 162 g/mol) to a methacryl functionality following the procedure outlined previously [2]. This 33% methacrylated TMTE, along with the other constituents, is illustrated in Figure 1.



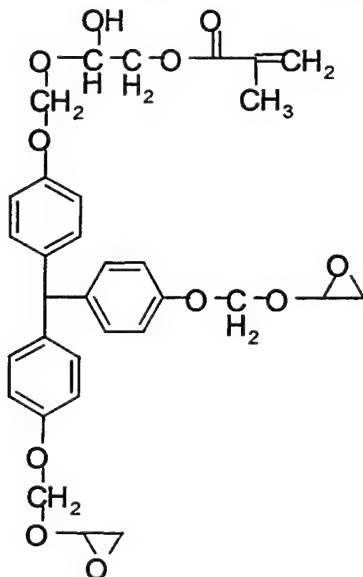
diglycidyl ether of bisphenol F (DGEBF) Epoxy



Bis(p-aminocyclohexyl) methane (PACM)



1,6-hexanediol dimethacrylate (HDDMA)



33% methacrylated triphenylmethane triglycidyl ether (33% TMTE)

Figure 1. IPN resin constituents.

3. Experimental

To study the influence of coupling between the DGEBF and HDDMA networks by the 33% TMTE the molar ratio of DGEBF to 33% TMTE was systematically varied from 4 mols of DGEBF to 0 mols of 33% TMTE (4-0 samples) through

0 mols of DGEBF to 4 mols of 33% TMTE (0–4 samples). Intermediate molar ratios of DGEBF:33% TMTE (3:1, 2:2, and 1:3) were also examined. The PACM concentration was always maintained at stoichiometry with respect to the DGEBF and 33% TMTE epoxy resins. The weight fraction of DGEBF and TMTE to HDDMA was maintained at a constant ratio of 0.70 to 0.30.

Two routes of curing the IPNs were pursued. The thermal cure conditions consisted of an initial cure at 70 °C for 3 hr, followed by cure at 140 °C for 2 hr, and a final post-cure at 250 °C for 1 hr. The two-stage curing schedule was selected to strictly control the formation of the epoxy-amine templated network. Previous research has shown that the Michael's addition side-reaction between the methacrylates and the PACM is minimal at 70 °C [2]. Therefore, the epoxy-amine stoichiometry is maintained. The e-beam cure route consisted of initial cure at 70 °C for 3 hr, followed by e-beam cure at a radiation dose of 20 Mrad, and a final post-cure at 250 °C for 1 hr.

Dynamic mechanical analysis (DMA) was performed using a TA Instruments 2980 DMA in the dual cantilever-bending mode. The samples were tested using a 20-mm frame and oscillatory displacement amplitude of 7.5 μm . The displacement amplitude was verified to ensure linear viscoelastic response by deriving corresponding stress-strain curves. The typical sample's width and thickness were approximately 12 mm \times 2 mm, respectively. Constant heating rate experiments were carried out at 2.0 °C/min, with a frequency of 1 Hz from 50° to 275 °C. Master curves were constructed from data obtained from multiple frequency sweeps, which were measured over three decades of frequency, ranging from 0.1 to 30 Hz in 3 °C isothermal steps. The glass transition temperatures were taken as the peak maximum of the loss modulus (E'') curves measured at 1 Hz. All samples were heated twice in the DMA. After the first heat, the samples were allowed to slow cool in the DMA to provide matching thermal histories. All DMA results in this report were taken from second heat measurements.

4. Results and Discussion

Figures 2–7 illustrate the dynamic mechanical response of the thermal and e-beam-cured samples at constant frequency (1 Hz) as a function of temperature. The overall trends in the dynamic mechanical properties are similar between the thermal and e-beam curing routes. In both cases, as the molar ratio of 33% TMTE to DGEBF is increased, the T_g is elevated and the glass to rubber transition zone is broadened. The trifunctional TMTE increases the crosslink density (ρ_c) of the cured IPN. An increase in the width of the distribution of segmental relaxation times is consistent with an increased ρ_c in highly crosslinked epoxy networks [3].

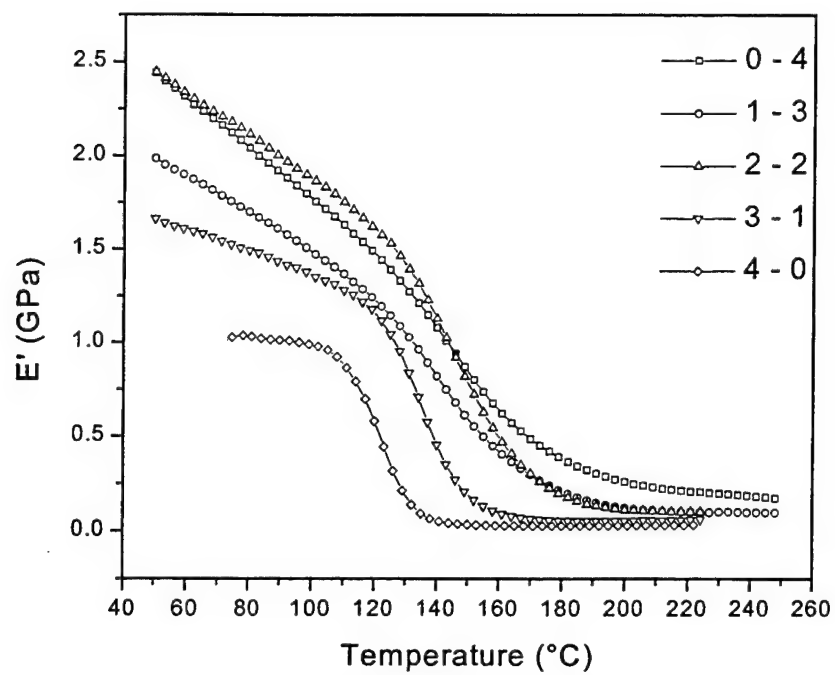


Figure 2. Storage modulus plots for thermal-cured IPNs.

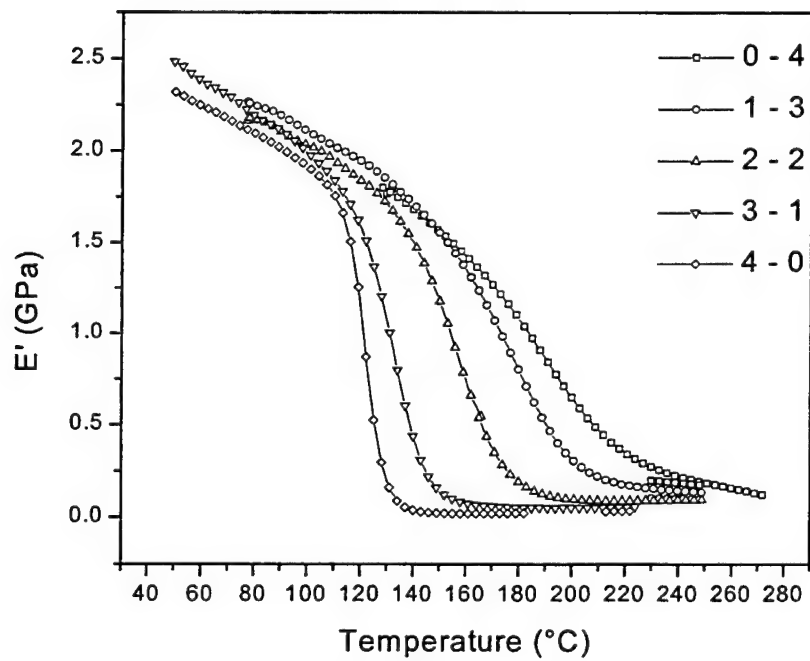


Figure 3. Storage modulus plots for e-beam-cured IPNs.

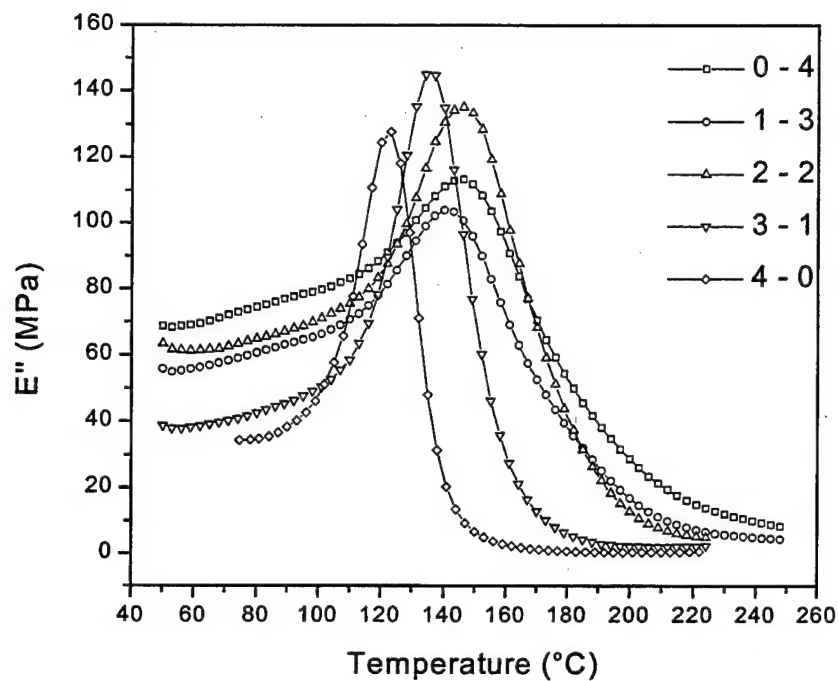


Figure 4. Loss modulus plots for thermal-cured IPNs.

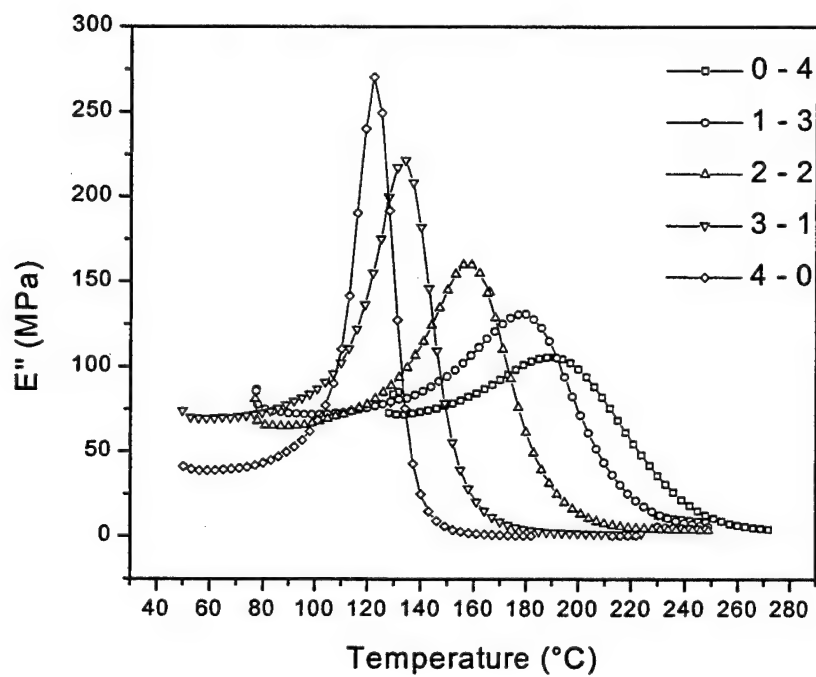


Figure 5. Loss modulus plots for e-beam-cured IPNs.

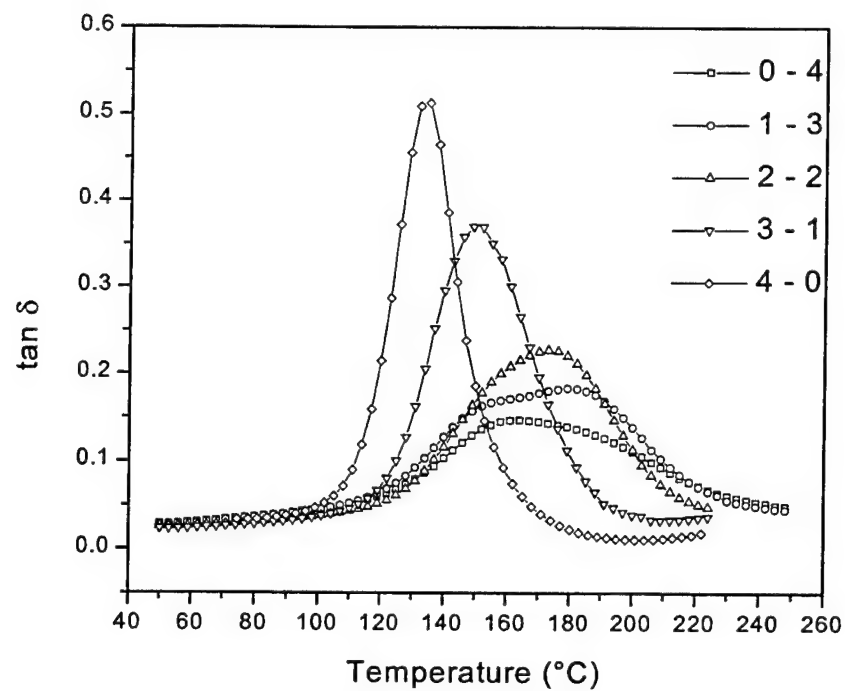


Figure 6. Loss tangent plots for thermal-cured IPNs.

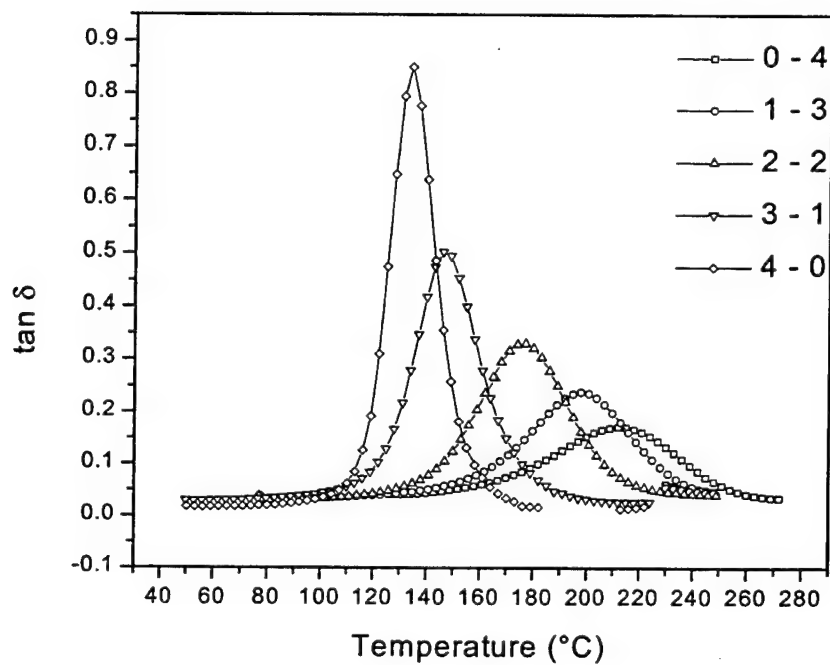


Figure 7. Loss tangent plots for e-beam-cured IPNs.

The 33% TMTE also covalently couples the epoxy-amine and free radical methacryl networks together, which increases the heterogeneity of molecular environments. This increase in T_g and breadth of the glass to rubber transition with increased coupling between the individual components of an IPN has been observed in other systems [4-7]. Akay and Rollins [4] determined that the broadening of the glass transition cannot be explained by a simple increase in crosslink density alone, and the coupling between the networks results in more complicated viscoelastic interactions. An apparent increase in crosslink density can be noticed in the rubbery regions of the storage modulus plots presented in Figures 2 and 3.

While the overall trends in the dynamic mechanical properties between the thermal- and e-beam-cured samples are similar, sufficient differences are present that merit further investigation. The e-beam-cured samples exhibit a steady rise in T_g from 122° to 190 °C, as seen in the E'' and $\tan \delta$ plots, as the molar ratio of the TMTE coupler is extended through the 4-0 to 0-4 samples, respectively. The T_g for the 4-0 (no coupler) thermal-cured samples is nearly identical to the e-beam counterpart at 123 °C, but the T_g values for the thermal route plateau at 145 °C beginning with the 2-2 sample. Fourier transform infrared (FTIR) results (not shown) indicate that the e-beam cure method achieves a greater degree of methacryl conversion than the thermal route, which results in the increased crosslink density and T_g for the e-beam-cured samples [2]. The depressed thermal conversion of methacryl functional groups is presumably due to the free radical propagation becoming restricted because of diminished molecular mobility as the thermal cure is advanced. It is interesting to note that the ultimate T_g reached during thermal cure of 145 °C closely matches the median thermal cure step of 140 °C. The thermal post-cure step at 250 °C increases the degree of methacryl conversion from 75-79% to 84-89%, but does not yield a further increase T_g . The e-beam-cured samples have a higher degree of methacryl conversion prior to post-curing (91-94%) and the additional post-cure step only increases the methacryl conversion by 2-4%.

The differences in glassy behavior between the thermal- and e-beam-cured IPNs are readily apparent as seen in Figures 2 and 3, respectively. The glassy storage moduli of the thermal-cured IPN vary greatly and rise from 1 GPa for the 4-0 sample to 2.5 GPa for the 0-4 sample. The glassy storage modulus of the e-beam-cured samples lies near 2.5 GPa for all of the samples regardless of the DGEBF to TMTE molar ratio. These results were also reproduced using another DMA [2], which adds weight to the argument that the differences in glassy response between the curing routes are real, and not instrument artifacts. Mobility in the glassy state is related to sub- T_g local secondary relaxation mechanisms such as the β transition [8]. The secondary β transition in epoxies based upon common diglycidylether of bisphenol A (DGEBA) is centered near -60 °C and is caused by

motion of the hydroxypropylether linkage and phenol ring flips [9]. The amplitude of the damping peak caused by the β transition has been found to be inversely proportional to the crosslink density at ambient temperatures in traditional microstructure networks, which results in a decreased glassy modulus [10-13]. A possible explanation proposed for this effect is that a crosslink point isolates short segments of network chain, therefore uncoupling local motion from other neighboring chain segments [11]. It has also been postulated that decreasing the cross-link density will decrease the glassy modulus due to weaker Van der Waals interactions [14]. The results obtained for this research point towards the uncommon trend in that the thermal-cured IPNs with the lowest ρ_c (4-0 sample with 84% methacryl conversion) have the lowest magnitudes of glassy modulus. The e-beam-cured IPNs all have similar methacryl conversions of 95-97% and similar glassy moduli. The thermal- and e-beam-cured IPNs have identical thermal histories after the post-cure step, so it is difficult to gauge the cause of the modulus differences (free volume, degree of conversion, IPN microstructure, etc.) without performing a detailed analysis of the β transition. On the basis of differences in glassy modulus between the e-beam and thermal-cured IPNs, one could also expect interesting differences in the sub- T_g nonequilibrium behavior [15]. This could lead to variations in the physical-aging rates between the e-beam and thermal-cured IPNs.

In addition to the differences in glassy modulus between the thermal- and e-beam-cured samples, significant changes in the $\tan \delta$ peak in the glass transition region are also apparent. Figures 6 and 7 illustrate the $\tan \delta$ plots as a function of DGEBF to TMTE molar ratio for the thermal- and e-beam-cured samples, respectively. The e-beam-cured sample displays a continuous shift in T_g towards higher temperatures with a corresponding broadening of peak width as the amount of TMTE is increased. The $\tan \delta$ curves for the e-beam samples are also relatively symmetric and are absent of any shoulders. As mentioned previously, the T_g of the thermal-cured 0-4, 1-3, and 2-2 samples plateau near 145 °C due to diffusion considerations. Shoulders in the $\tan \delta$ signals of the thermal-cured 1-3 and 0-4 samples also appear that are not evident in the corresponding e-beam samples. The observation of a shoulder or second peak in the DMA spectra of an IPN is caused by multiple molecular relaxation mechanisms of multiple phase domains [5, 16].

However, it is difficult to ascertain the molecular origin of the relaxation mechanism responsible for the $\tan \delta$ shoulders present in the thermal-cured 1-3 and 0-4 samples from the simple isochronal DMA measurements performed for Figure 6. An alternative approach to enhance the shoulder region of the $\tan \delta$ peaks is to sweep the frequency (f) of the DMA measurement at isothermal temperatures. This method has been used successfully to separate the overlapping β -transition of an epoxy matrix from the low temperature α -transition of an included rubber toughener [17]. The peak-shoulder separation

achieved during this type of frequency sweep is improved for overlapping molecular processes that differ greatly in Arrhenius activation energy (E_a), as described by equation (1):

$$\ln\left(\frac{f}{f_o}\right) = -\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right), \quad (1)$$

where

T = the temperature (in degrees Kelvin) of the peak maximum, and
 T_o = the reference temperature.

Figures 8 and 9 show the isothermal frequency sweep E'' and $\tan \delta$ plots for the e-beam-cured 1-3 sample, respectively. Again the e-beam-cured 1-3 sample displays a single homogeneous transition with no shoulders. The E'' peaks range in temperature from approximately 170° to 190 °C as the frequency of the measurement is swept from 0.1 to 30 Hz, respectively. The corresponding $\tan \delta$ signal peaks are roughly 20 °C greater than the loss modulus peaks.

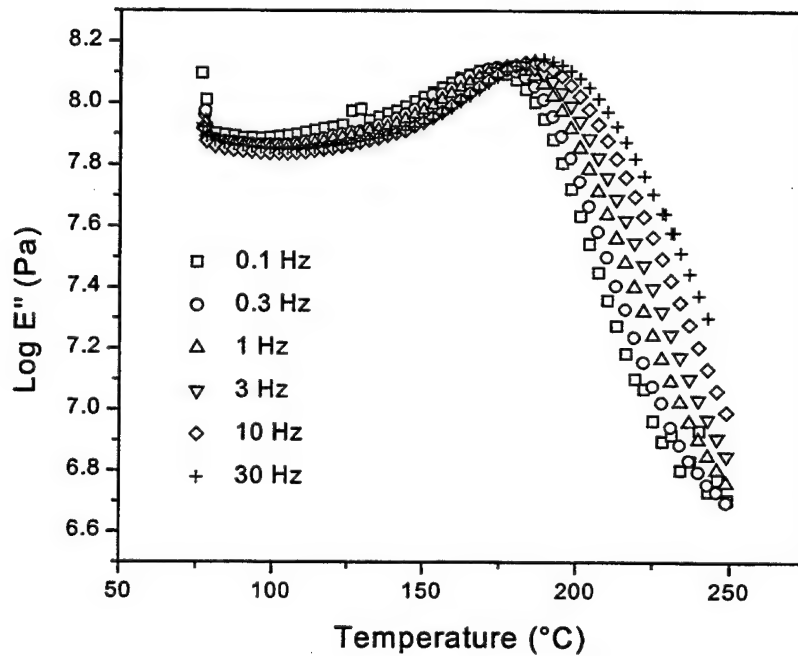


Figure 8. Loss modulus frequency sweep measurements of e-beam-cured 1-3 sample.

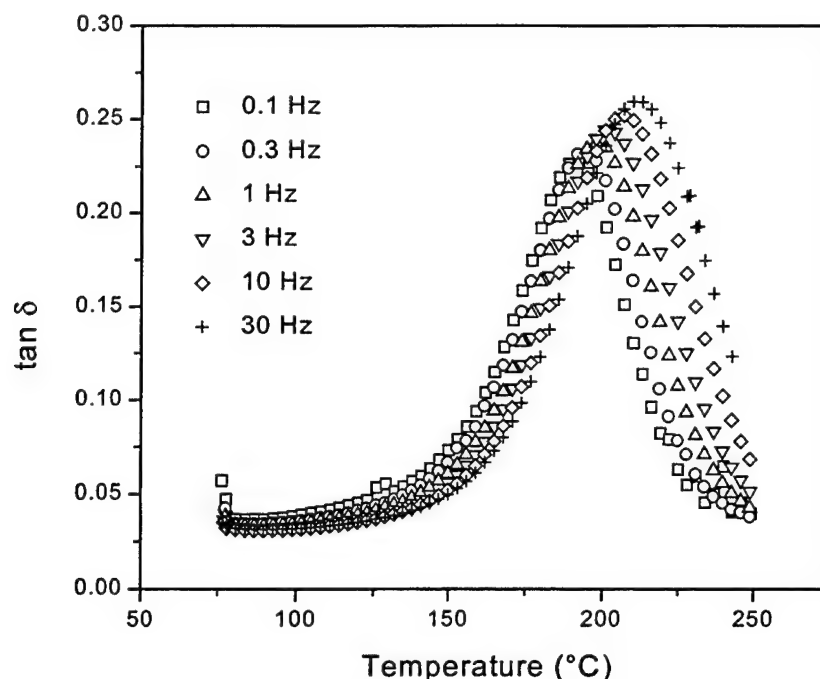


Figure 9. Loss tangent frequency sweep measurements of e-beam-cured 1-3 sample.

In contrast to the e-beam-cured 1-3 sample, E'' shoulders are still evident in the multiple frequency-sweep plots of the thermal-cured 1-3 sample (Figure 10) at high temperatures trailing the peak maxima ($\sim 190^{\circ}$ – 210° °C), but are not shifted from the main loss modulus peaks at any measured frequency. Therefore, the molecular mechanism responsible for the loss modulus shoulder in the thermal case must have an Arrhenius activation energy nearly identical to the primarily observed transition. Furthermore, when the loss modulus curves of Figure 10 and the $\tan \delta$ curves of Figure 11 are directly compared, an interesting observation is noted. The primary transition present in the E'' curves ($\sim 135^{\circ}$ – 155° °C) correlate to the leading shoulders in the respective $\tan \delta$ curves. The trailing shoulders in the E'' curves ($\sim 190^{\circ}$ – 210° °C) link to the primary peaks in the $\tan \delta$ curves. The difference in temperature between analogous E'' and $\tan \delta$ peaks for the thermal-cured 1-3 samples is nearly 40 °C. This raises more suspicion that the observed relaxations near 140°–145 °C for the higher crosslink density thermal samples are due to memory retention of the median oven-cure stage.

Cure memory in the dynamic mechanical glass transition has been observed in polyamidoamine-epoxy networks by other researchers [18]. Sanz et al. [19] also observed shoulders in the $\tan \delta$ signals of stoichiometric epoxy-amine systems with temperatures and magnitudes dependent upon the thermal-cure conditions. This is a result of a fraction of the network structure attaining a high-crosslink density during gelation at the median-cure stage. During the post-cure stage,

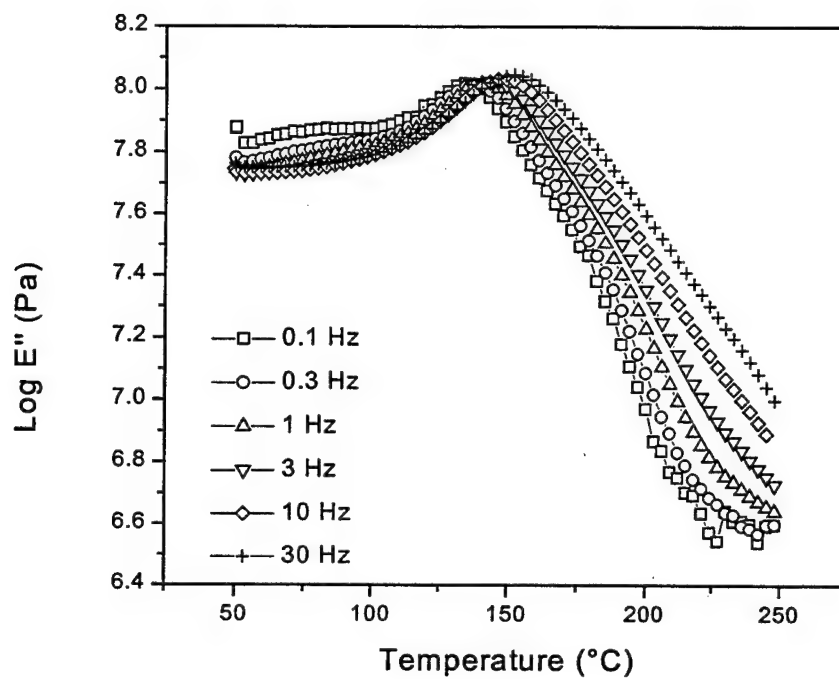


Figure 10. Loss modulus frequency sweep measurements of thermal-cured 1-3 sample.

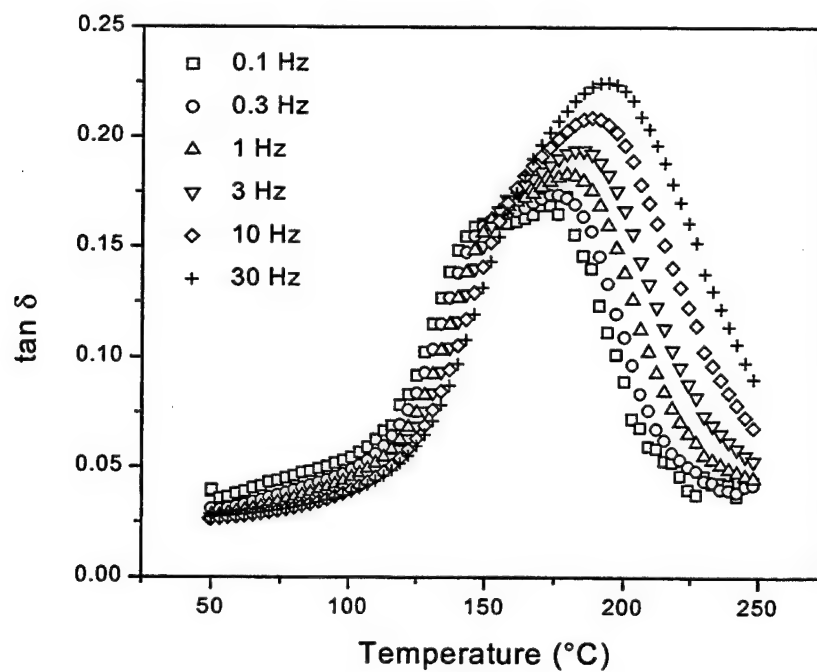


Figure 11. Loss tangent frequency sweep measurements of thermal-cured 1-3 sample.

further crosslinking reactions occur, but are diffusion limited within these regions of high-crosslink density from the previous cure stage. The physical heterogeneity between these regions of low- and high-crosslink density results in the broadness observed in the E'' curves during DMA experiments. The broadness in the E'' curves for the thermal-cured IPNs appears to be caused by physical mechanisms. In the case of the thermal-cured 1-3 samples, the E_a calculated from the primary loss modulus peaks (135°-155 °C range) is 477 kJ/mol and 456 kJ/mol from the $\tan \delta$ peaks (175°-195 °C range). These values are very close to E_a values of 498 kJ/mol and 509 kJ/mol calculated for the e-beam 1-3 E'' and $\tan \delta$ signals, respectively.

A goal of this research was to investigate the possibility of using DMA to correlate the observed densities and cure shrinkage of the IPN adhesives to free volume. Gerard et al. [20] have used this approach to relate the crosslink density and chain flexibility of model epoxy-amine networks to free volume. Akay and Rollins [4] also examined the free-volume and glass-transition broadening of polyurethane/poly (methyl methacrylate) IPNs from viscoelastic standpoint. For this research, the viscoelastic interpretations were derived from a similar perspective using master curves of the loss modulus, which were constructed in the frequency (ω) domain in the glass transition region ($T_g \pm 30$ °C) following the time-temperature superposition principle (tTsp) [3]. Prior to shifting the modulus isotherms horizontally along the frequency axis, a vertical shift factor correction of T_0/T was applied, where T_0 represents the reference temperature. The horizontal shift factors ($a_T > T_g$) were then fitted to the empirical and free volume derived Williams-Landel/Ferry (WLF) equation (2). The WLF equation is used to describe the temperature dependence of the distribution of relaxation times (τ) in viscoelastic materials. The C_1 and C_2 constants of the WLF equation were determined using a nonlinear least squares fit. The fractional free volume at the glass transition (f_g) and coefficient of thermal expansion of the fractional free volume (α_f) were then solved using the C_1 and C_2 constants and setting empirical Doolittle constant (B) equal to 1 [20, 21]. The C_1 and C_2 constants of the WLF equation can also be used to solve for E_a . The breadth of the distribution of relaxation times was quantified by fitting the master curves to the Kohlrausch-Williams/Watts (KWW) equation (5) and determining the coupling parameters (β) [22]. The β parameters were found using the methodology outlined by Weiss et al. [23, 24].

$$\log a_T = \log \frac{\tau^*}{\tau_0^*} = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (2)$$

$$C_1 = \frac{B}{2.3f_g} ; C_2 = \frac{f_g}{\alpha_f} \quad (3)$$

$$E_a = -2.303RT^2 \frac{d \log a_T}{dT} . \quad (4)$$

$$\phi(t) = \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] \rightarrow 0 < \beta \leq 1 . \quad (5)$$

Figures 12 and 13 show the E'' master curves and KWW fits for the thermal and e-beam-cured samples, respectively. For each sample, the isotherms successfully shifted to form smooth and continuous master curves. The KWW equation also provided reasonable descriptions of the master curves, with the β parameters summarized in Table 1. For each cure route, it can be seen that the breadth of the E'' master curves with increased TMTE concentration. This increase in coupling between networks and subsequent increase in crosslink density is reflected as a decrease in the β parameters (0.237 for the e-beam 4-0 sample to 0.113 for the e-beam 0-4 sample and 0.202 for the thermal 4-0 sample to 0.113 to the 0-4 thermal sample). The reference relaxation time used for the KWW fits is also provided.

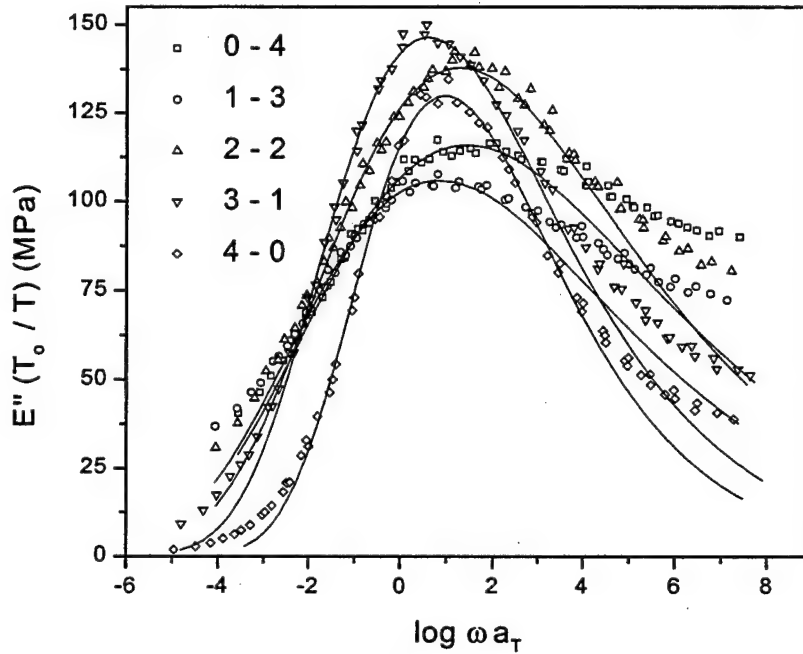


Figure 12. Loss modulus E'' master curves and KWW fits for thermal-cured samples.

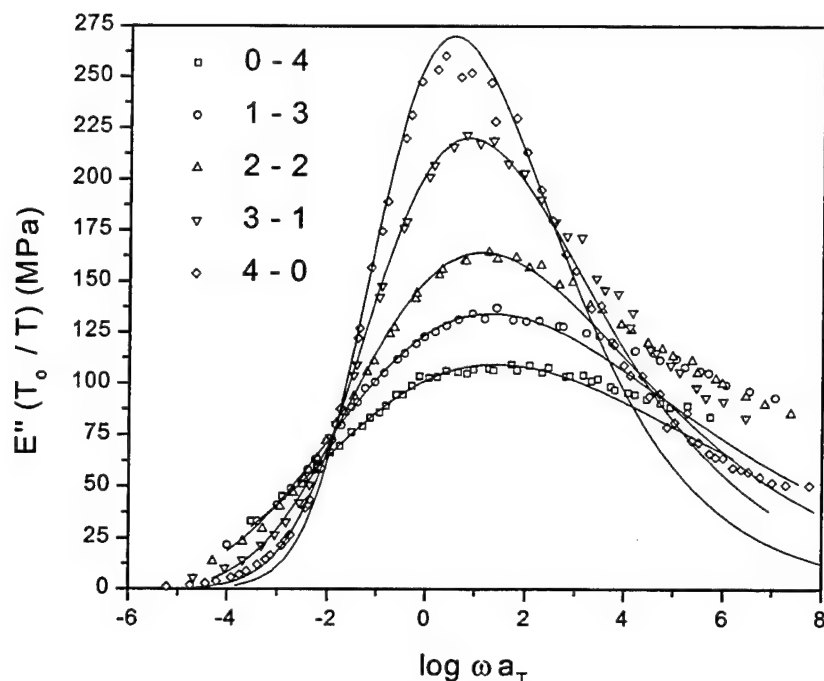


Figure 13. E'' master curves and KWW fits for e-beam-cured samples.

However, for tT_{sp} to be gauged a success, the shift factor plots and WLF parameters must also be considered. Table 1 also summarizes T_g , E_a , C_1 , C_2 , f_g , and α_f . Figures 14 and 15 show the shift factor plots for the thermal and e-beam-cured samples, respectively. The values calculated for the thermal-cured 0-4, 1-3, and 2-2 samples must certainly be incorrect as multiple relaxation processes were clearly observed in the E'' and $\tan \delta$ signals [3]. This can also be seen in the shift factor plots (Figure 14), as the curves for these samples were nearly linear and deviated from WLF behavior. The thermal-cured 2-2 sample fits the WLF equation so poorly that none of the parameters could be reasonably determined or approximated. The WLF parameters obtained for the thermal-cured samples with little inter-network coupling, 4-0 and 3-1, seemed reasonable.

The most interesting viscoelastic behavior is observed in the e-beam-cured IPN where no directly observable multiple relaxation peaks or shoulders were found in the E'' and $\tan \delta$ signals. The shift factor plots for the e-beam-curing process (Figure 15) are similar to the thermal-cured counterparts in that as the molar ratio of TMTE coupler to DGEFB is increased, the temperature sensitivity of $\log a_T$ decreases. This result is consistent with the results of Ogata et al. [25], where a decrease in the temperature and frequency dependency of the glass to rubber relaxation for phenol-formaldehyde novolac epoxy networks was found as the crosslink density was increased. Significant departures from typical epoxy-amine network properties are found in the values of f_g and α_f calculated for the e-beam-cured IPNs. The uncoupled 4-0 sample has values of f_g and α_f that are in the range

Table 1. Viscoelastic parameters derived from fits of master curves.

Sample	$\beta \times 10^1$	$\tau \times 10^2$ (s)	T_g (°C)	E_a^a (kJ/mol)	E_a^b (kJ/mol)	C_1	C_2 (°C)	$f_g \times 10^2$	$\alpha_f \times 10^4$ (°C ⁻¹)
E-beam									
0-4 E	1.13	0.38	190	472.2	484.4	47.1	399.1	0.92	2.3
1-3 E	1.25	0.48	181	497.0	623.6	19.8	125.3	2.2	1.8
2-2 E	1.53	0.75	158	627.5	642.3	17.1	94.7	2.5	2.7
3-1 E	1.92	1.4	134	597.7	710.2	13.3	59.4	3.3	5.5
4-0 E	2.37	2.9	122	631.9	902.8	11.0	36.4	4.0	10.6
Thermal									
0-4 T ^c	1.15	0.35	145	440.4	443.9	22.9	172.6	1.9	1.1
1-3 T ^c	1.25	1.4	141	477.3	614.0	11.9	63.6	3.7	5.7
2-2 T ^c	1.31	0.5	145	501.4	c	c	c	c	c
3-1 T	1.70	2.5	135	659.6	709.4	14.8	66.5	2.9	4.4
4-0 T	2.02	1.1	123	623.1	699.8	14.8	63.5	2.9	4.6

^aArrhenius.

^bWLF.

^cMultiple transitions observed in loss modulus spectra.

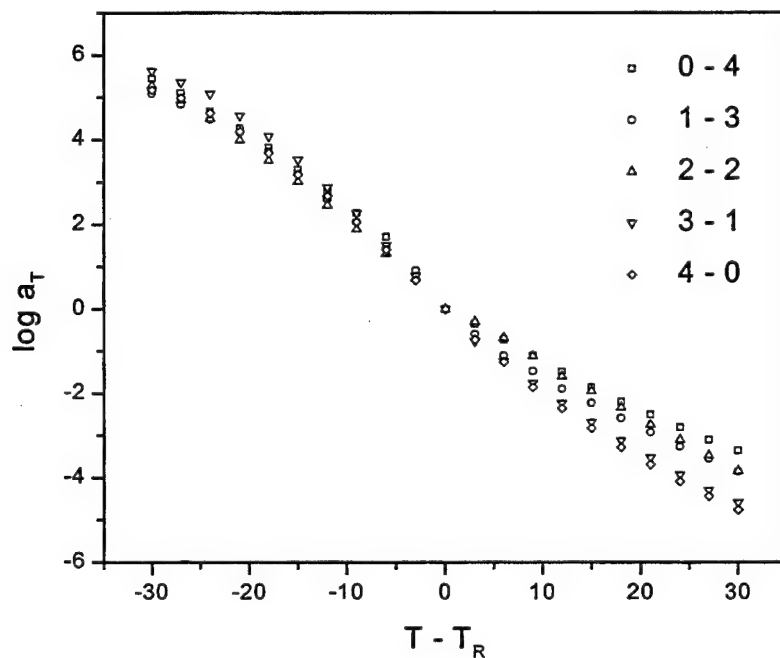


Figure 14. Shift factor plots for thermal-cured IPNs.

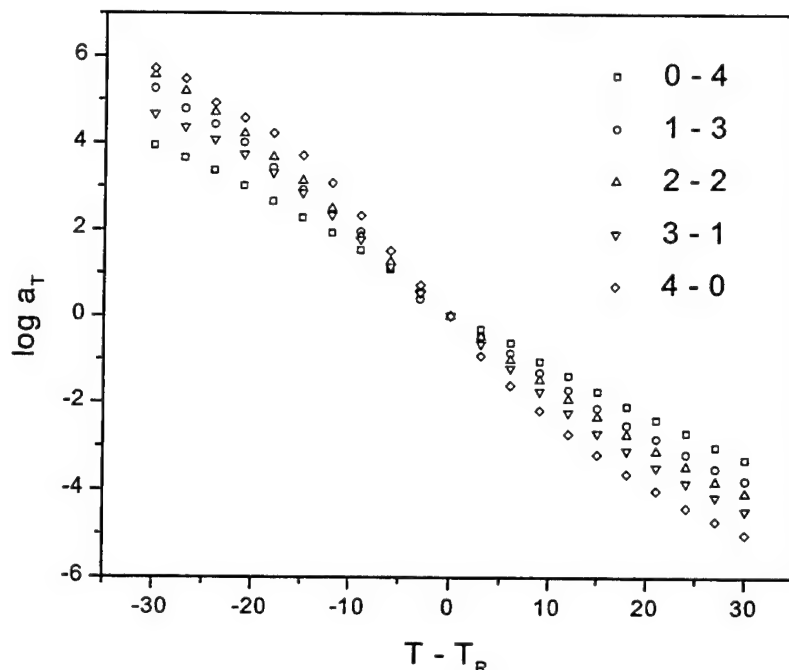


Figure 15. Shift factor plots for e-beam-cured IPNs.

of values for conventional thermosets, as determined by Gerard et al. [20]. As the molar ratio of TMTE to DGEBF is increased, the calculated values of f_g and α_f decrease significantly. The most coupled sample (0-4) has an α_f value in the rubbery region, which is an order of magnitude lower than the typical values reported by Gerard. This inter-network coupling profoundly increases the overall crosslink density of the IPN. One must also keep in mind that the viscoelastic response of the highly coupled e-beam IPN samples also deviates considerably from ideal WLF behavior, so the assumption of a single relaxation mechanism may not be valid. While it is uncertain whether or not multiple relaxation mechanisms from a heterogeneously crosslinked network structure are active in the case of the e-beam-cured IPNs, the trends in the viscoelastic data point towards a more homogeneously crosslinked network in comparison to the thermal-cure counterpart.

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List of Acronyms and Abbreviations

a_T	WLF isothermal shift factor
B	Doolittle equation parameter
β parameter	KWW equation fitting parameter
β transition	localized glassy polymeric sub- T_g relaxation
$^{\circ}\text{C}$	degrees Celcius
C_1	WLF fitting parameter
C_2	WLF fitting parameter
DGEBA	diglycidyl ether of bisphenol A
DGEBF	diglycidyl ether of bisphenol F epoxy resin
DMA	dynamic mechanical analysis
E'	dynamic storage modulus
E''	dynamic loss modulus
E_a	Arrhenius activation energy
e-beam	electron beam
EEW	epoxy equivalent weight
f_g	fractional free volume at $T = T_g$
FTIR	Fourier transform infrared spectroscopy
GPa	giga Pascals
HDDMA	1,6-hexanediol dimethacrylate
IPN	interpenetrating polymer network
KWW	Kohlrausch-William/Watts equation
mm	millimeters
MPa	mega Pascals
PACM	bis (p-aminocyclohexyl) methane
T	temperature
T_g	glass transition temperature
T_0	WLF equation reference temperature
$\tan \delta$	E''/E'

tTsp	time-temperature superposition principle
TMTE	triphenylolmethane triglycidyl ether
WLF	Williams–Landel/Ferry equation
4-0	4 mols of DGEBF epoxy to 0 mols of 33% TMTE
3-1	3 mols of DGEBF epoxy to 1 mols of 33% TMTE
2-2	2 mols of DGEBF epoxy to 2 mols of 33% TMTE
1-3	1 mols of DGEBF epoxy to 3 mols of 33% TMTE
0-4	0 mols of DGEBF epoxy to 4 mols of 33% TMTE
α_f	coefficient of thermal expansion of the fractional free volume
μm	micrometers
ω	angular frequency
ρ_c	crosslink density
τ	relaxation time constant of KWW equation

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